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13. ABSTRACT (Maximum 200 words) Report developed under SBIR contract. We have prepared a series of hybrid additives and incorporated them into urethane and epoxy coatings that were applied on steel and aluminum substrates. The films were homogeneous, but with a high coefficient of friction. The resulting coating toughness was increased, as measured by the improved abrasion resistance, hardness and flexibility of the coating. Similarly, the oxygen index and smoke density properties of the coating were used to demonstrate improved fire resistance. Corrosion was measured by the Salt Fog test, and used to demonstrate that these additives inhibit rust formation and propagation. The addition of hybrids to the coatings provided some thermal stability to the system, leading to reduced thermal degradation at high temperatures (200 to 400°C). An engineering analysis demonstrated that the additives can be prepared at \$1-\$2/lb, well below the price of specialty additives like corrosion inhibitors and UV stabilizers.		
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# **Non-Skid, Non-Flammable Coating for Navy Applications**

## **Phase I Final Report**

by:

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For:  
**Naval Sea Systems Command**  
Contract No. N00024-98-4087  
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## Project Summary

**Purpose of the Research:** Non-skid coatings for Navy and other marine applications are traditionally made with urethane and epoxy resin formulations that have a very high content of hard, abrasive particles. The U.S. Navy uses these coatings on aircraft carrier decks to provide frictional resistance to the landing surface and has specified a military standard to meet its requirements (MIL-PFR24667A). However, currently available coatings do not meet these specifications. The coatings wear out and have to be replaced after 3,000 to 6,000 landings, instead of the specified 10,000 landings. Arresting cables on flight decks cause a significant amount of physical wear and damage to the coating. Additionally, corrosion of the deck surface from the constant exposure to salt water, along with chemical degradation caused by jet fuels and oils, leads to material failure and the need to frequently replace the coating. Other requirements of non-skid coatings include low flammability and smoke generation during a fire. A tough, wear-resistant non-skid coating is needed with significant improvement in properties like strength, chemical and fire resistance, in order to meet and exceed the military specifications.

**Description of the Research:** TDA Research, Inc. (TDA) has proposed to incorporate alumoxanes into the base polymer to make hybrid organic/inorganic resins that resist wear and damage caused by arresting cables on carrier decks. Alumoxanes are nanoparticles that can react with and bond directly into the urethane and epoxy polymer framework, introducing a strong and abrasion resistant inorganic component to the resin system. As well dispersed, chemically bonded, high surface area particles, alumoxanes minimize crack propagation and improve the toughness of the coating. Since alumoxane polymers also have good barrier properties, they can provide a significant improvement in the corrosion resistance and flame retardancy.

**Research Findings:** We have successfully prepared several alumoxanes and incorporated them into urethane and epoxy resin systems, as shown in Figure 2. Reactive alumoxane diols and amines were synthesized and characterized. New alumoxanes designed to impart special properties like fire retardance to the coating were also synthesized. The tailored properties were achieved by using two different carboxylic acids on the boehmite nanoparticle, one acid to attach the alumoxane to the resin system, the other to provide the fire retardant properties. These "mixed acid alumoxanes" served to chemically bond phenolics to the resin, improving properties like fire resistance. An inexpensive synthesis of alumoxanes was identified using the commercially available mineral boehmite, instead of the costly sol-gel process. Thus the preparation of alumoxanes was carried out in a one-pot synthesis, bringing the cost of the reactive to less than \$2/lb.

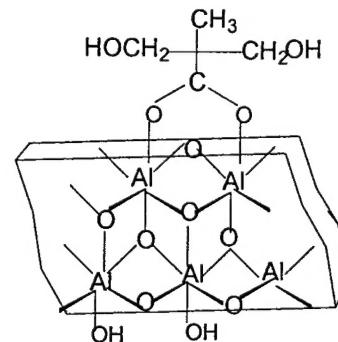


Figure 1. The alumoxane structure with boehmite and a carboxylic acid.

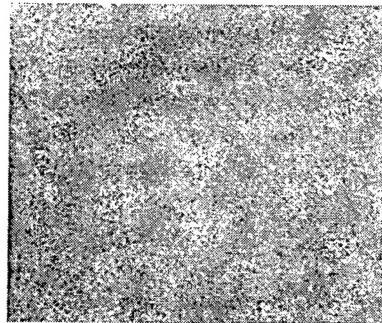


Figure 2. Homogeneous coating with 50% alumoxane.

Coatings were prepared using commercial formulations, such as International Paint's urethane Proreco marine coatings. Spectroscopic methods were used to confirm that the alumoxane was chemically bound to the resin and thus an integral part of the coating. We also incorporated alumoxanes in commercial pigmented paint and a highly filled non-skid coating, and found them to be compatible with both systems. The alumoxane resins were applied to steel and aluminum substrates by conventional methods and no new, costly equipment was necessary.

The coating toughness was significantly increased by the incorporation of alumoxanes. Properties such as abrasion resistance, hardness and flexibility were enhanced in preparations that had 10% to 50% of the hybrid material. Thus mechanical wear from arresting cables should be significantly reduced. The nanoparticles also provided good frictional resistance and non-skid properties, exceeding the military specification. Thermal degradation studies of the coating demonstrated that alumoxanes had a stabilizing influence; coatings exposed to 400°C in air experienced significantly less weight loss than that measured with commercial coatings. Thermal degradation is caused by aircraft exhaust systems and compressors.

The chemical properties of the coating were also significantly improved. Salt Fog tests demonstrated that alumoxanes provide a high degree of corrosion resistance. Additionally, exposure to jet fuel, pump oil and acetic acid did not compromise the properties of the coating. As for the fire retardant properties of the coating, the addition of alumoxanes resulted in a lowering of smoke generation under flaming and non-flaming conditions. At a high loading of alumoxanes, flammability was reduced, as indicated by the high oxygen concentration required to sustain a flame.

**Cost Analysis.** An engineering analysis was conducted to evaluate the market feasibility of using alumoxanes to make non-skid coatings. Including the materials and manufacturing costs, alumoxanes are expected to cost \$1-2/lb, a price that is competitive with the fillers and additives currently used in the coatings industry. Fillers like colloidal silica sell for \$4-\$6/lb, while aluminum fillers start at \$2/lb. Since alumoxanes can also act as fire retardants and corrosion inhibitors, the overall cost savings would be substantial.

**Potential Applications:** These include non-skid coatings for marine applications such as carrier decks and small boat surfaces. Architectural applications include swimming pool decks, floors, stairways in patios and garages.

**Commercialization:** TDA has been working with Air Products and Chemicals (APCI) at Allentown, PA to develop alumoxanes. TDA has entered into agreements with APCI to market and sell the alumoxanes as reactive additives. International Paint, one of the largest producers of specialty coatings, including marine coatings, is interested in the TDA's alumoxane technology. Finally Newport News Shipbuilding, the largest consumer of Navy non-skid coatings is also interested in alumoxane coatings for its applications.

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## Table of Contents

<b>Non-Skid, Non-Flammable Coating for Navy Applications.....</b>	<b>i</b>
<b>Project Summary .....</b>	<b>ii</b>
<b>1. Introduction.....</b>	<b>1</b>
1.1. Problem and Approach.....	1
1.2. Background .....	2
1.3. Phase I Objectives .....	4
<b>2. Results of Phase I Project.....</b>	<b>5</b>
2.1. Task 1. Synthesis and characterization of alumoxane precursors .....	6
2.2. Task 2. Incorporation of alumoxanes into non-skid coatings .....	9
2.3. Task 3. Testing the alumoxane non-skid coatings.....	10
2.3.1. Toughness .....	11
2.3.2. Flammability and Thermal Properties.....	13
2.3.3. Corrosion resistance .....	16
2.3.4. Chemical resistance .....	16
2.4. Task 4. Choosing the best candidate and providing samples to Naval facility .....	17
<b>3. Phase II Objectives .....</b>	<b>19</b>
3.1. Phase II Technical Objectives .....	19
3.2. Phase III Commercialization.....	20
<b>4. Commercial Potential .....</b>	<b>20</b>
<b>5. Summary and Conclusions.....</b>	<b>21</b>
<b>6. References .....</b>	<b>21</b>

## List of Figures

Figure 1. The alumoxane structure with boehmite and a carboxylic acid. ....	ii
Figure 2. Homogeneous coating with 50% alumox-ane. ....	ii
Figure 4. Preparation of alumoxane from boehmite and organic acids .....	2
Figure 3. Examples of alumoxanes prepared at TDA. a) dimethylol propionic acid b) lysine c) hydroxybenzoic acid d) amino benzoic acid alumoxanes.....	2
Figure 5. Reaction of alumoxane to give a nanocomposite urethane. ....	3
Figure 6 A mixed acid alumoxane.....	3
Figure 7.Crack propa-gation through filled resins.....	4
Figure 8. Structures of alumoxanes with phenolic groups. ....	7
Figure 9. FT-IR spectra of diphenolic acid (DPA and alumoxane-DPA .....	7
Figure 10. TGA of HD Alumoxane. ....	8
Figure 11. XRD of mixed acid alumoxane.....	9
Figure 12. Coatings showing wear by Tabor Test. Clear coating (left) alumoxane coating (right).12	12
Figure 13. $\mu_s$ versus alumoxane content. ....	13
Figure 14. Weight loss as thermal degradation measured by TGA. ....	14
Figure 15. Influence of alumoxane content on thermal degradation of the coating. ....	14
Figure 16. Panels exposed to Salt Fog tests (a) urethane coating after 600 hours (b) 30% alumoxane in urethane after 600 hours (c ) 40% alumoxane in urethane after 1300 hours.16	16

## List of Tables

Table 1. Composition of mixed acid alumoxanes .....	8
Table 2. Coatings prepared with alumoxane HD10.....	9
Table 3. Coatings prepared with alumoxane HD50.....	10
Table 4. Coatings prepared with alumoxane HD30.....	10
Table 5. Coatings prepared with alumoxane DD10.....	10
Table 6. Coatings prepared with commercial non-skid Proreco 469 and alumoxane HD10. ....	10
Table 7. Pencil hardness of alumoxane resins (ASTM 3363). ....	11
Table 8. Thickness loss after several cycles on the Tabor Abraser by ASTM 4060 (measured in mil). ....	12
Table 9. Thermal properties of the coating measured by DSC.....	13
Table 10. Weight loss from the thermal degradation of alumoxane coatings over a wide range of temperatures. ....	15
Table 11. Smoke Density values for alumoxane coatings .....	15
Table 12. Oxygen Index of alumoxane coatings. ....	16
Table 13. Chemical resistance of alumoxane coatings, measured by pencil hardness, according to ASTM D1308. ....	17
Table 14. Summary of phase I results. Prperties of alumoxane coatings.....	18

## 1. Introduction

### 1.1. Problem and Approach

Non-skid coatings have the dual purpose of protecting the steel substrate on an aircraft carrier deck from the elements while serving as a surface with high frictional resistance. The protective functions of a coating are particularly important for the US Navy as it operates in the highly corrosive environments of salt water, sun, wind and rain. Non-skid coatings are particularly challenging on landing decks of aircraft carriers, where landing aircraft require a coating with a consistently high frictional resistance, but with superior toughness to reduce the physical damage caused by arresting cables. Current highly filled organic coatings provide some protection from the elements, while giving the deck surface non-slip properties. However, these coatings easily chip off, releasing particulate fillers and losing their protective film characteristics. Accelerated wear of the organic coating by arresting cables shortens the lifetime of the deck coating to some 3,000 to 6,000 landings, far short of the MIL24667A requirement of 10,000 landing. Therefore, a new type of tough and wear-resistant non-skid coating is necessary to meet and exceed the current military standard.

Coatings also protect the deck surface from corrosion that results from continuous exposure to salt water over a broad range of temperatures. Often the coating is replaced because mechanical wear or chemical degradation compromises its protective capability. The relatively poor resistance of a deck coating towards organic solvents, aviation fluids and lubricating oils, is also a problem. Finally, in the presence of so many combustible fluids, it is imperative that the coating has superior flame resistance.

Traditionally, the non-skid properties have been achieved by adding inorganic particles like silica and alumina to the coating. Hard and highly abrasive particles, including aluminum and crystalline silica, give a coating with a high coefficient of friction. More recently, polymeric materials, such as polybutadiene rubber and polyethylene particles have been used to increase the coefficient of friction (Burnside 1995). These hard additives provide frictional resistance by protruding from the coating, but chip off under high shear forces, compromising the integrity of the film. The US Navy uses non-skid urethane and epoxy coatings with silica, aluminum and polymeric particles on aircraft carrier decks, ordinance, landing mats and bridges.

The use of an arc-sprayed aluminum coating, with a high coefficient of friction, is an innovative approach to a non-skid coating, but it has proven to be very expensive to apply and difficult to repair (Hare 1997, Sulit 1994). A significant improvement in toughness and coating durability has been achieved with the addition of colloidal silica to the coating, with particles ranging from 10 to 150 nanometers. However, these nanoparticle dispersions are very pH sensitive and difficult to incorporate into organic coatings; they are also very expensive (\$4-\$6/lb).

Ideally, a non-skid coating should provide superior frictional resistance, be inexpensive and easy to apply. It should also provide good corrosion protection, low flammability and superior toughness in order to extend its useful lifetime. This can be achieved by making a coating system in which well dispersed inorganic nanoparticles are chemically bound into the polymer to provide traction and corrosion resistance, without the cracking and chipping found with conventional fillers. Material toughness is dramatically improved by the addition of nano-sized

( $10^{-9}$  m) particles, increasing the coating's mechanical strength and wear resistance (Kubouchi 1996, Azami 1996). Additionally, fire resistance is markedly enhanced by the incorporation of a self-extinguishing inorganic component as part of the polymeric framework. Inorganic nanoparticles form an excellent fire retardant layer, acting as a barrier to gases that propagate a fire. Finally, the good barrier properties provided by the inorganic component also improve the chemical resistance of a coating and reduce corrosion.

In this Phase I project, TDA has demonstrated that the use of a hybrid organic/inorganic reactive additive can provide a coating with high frictional resistance while improving its toughness. We have combined the excellent film forming properties of organic coatings with the superior corrosion and fire resistance of inorganic aluminum systems to prepare a coating with excellent corrosion protection and mechanical properties. The non-skid, abrasion-, crack- and corrosion- resistance is achieved by the incorporation of alumoxanes into the coating. Alumoxanes are inorganic boehmite nanoparticles  $[\text{Al}(\text{O})(\text{OH})]$ , chemically bound to the polymer coating through functionalized organic molecules. They are prepared by reacting boehmite with carboxylic acids, as shown in Figure 4 (Kimura 1987). Unlike conventional fillers, alumoxane nanoparticles are chemically bound into the polymer network, greatly enhancing the dimensional, chemical and thermal stability of the coating (Landry 1995, karieve 1992).

## 1.2. Background

Functionalized carboxylato alumoxanes are hybrid organic/inorganic reactive additives that can be incorporated into a coating to improve specific properties such as toughness, corrosion resistance and fire retardancy, while increasing frictional resistance. These are desirable properties for a non-skid coating designed for marine applications; they include flight decks on aircraft carriers, landing mats, bridges and ordinance. The alumoxanes prepared at TDA are hybrid nanoparticles that are homogeneously dispersed and chemically bound to the polymer framework of the coating. Thus, the inorganic nanoparticle becomes an integral part of the coating film, providing increased hardness, impact and abrasion resistance, thereby improving the toughness of the coating and increasing its useful lifetime.

The alumoxanes are low-cost hybrid organic/inorganic monomers prepared in a one step synthesis from boehmite, a natural mineral, and an organic acid (Landry 1995). Some of the alumoxanes prepared at TDA include dimethylol propionic acid, lysine, hydroxybenzoic acid and amino benzoic acid alumoxanes, shown in Figure 3. When the acid

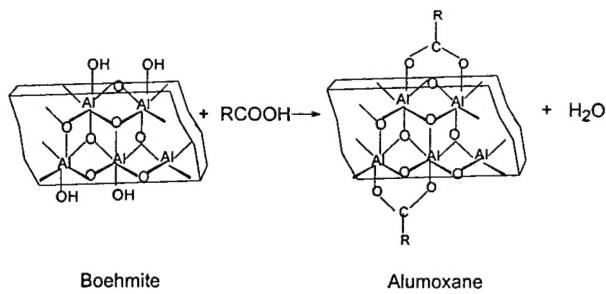


Figure 4. Preparation of alumoxane from boehmite and organic acids

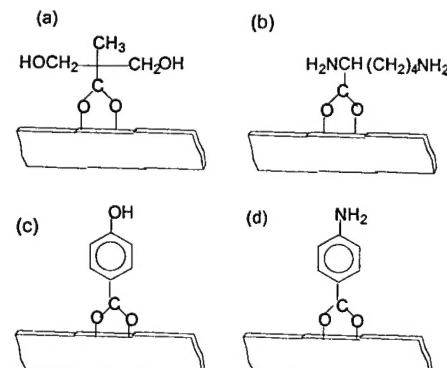


Figure 3. Examples of alumoxanes prepared at TDA. a) dimethylol propionic acid b) lysine c) hydroxybenzoic acid d) amino benzoic acid alumoxanes.

has a reactive functional group like an amino group or a hydroxyl group, the alumoxane can be chemically bound to a polymeric resin, like a urethane or an epoxy, as shown in Figure 5. The physical and chemical properties of the alumoxanes can be controlled by the choice of organic molecule, and range from water soluble powders to hard solids that are resistant to acids, bases and organic solvents (Lam 1992, Whiteside 1991). The inorganic component provides the toughness and high frictional resistance necessary for non-skid coatings, while the organic component provides processing flexibility and excellent film forming properties (Schubert 1995). By covering the boehmite particle with the appropriately functionalized carboxylic acids, the alumoxanes can be incorporated into urethanes, epoxies, acrylics and polyesters to give clear films for applications that include adhesives and coatings.

Functionalized alumoxanes (alumoxanes with functional groups used to bind the nanoparticle to the polymer resin) have been prepared at TDA using dimethylol propionic acid (DMPA), whereby the carboxylic acid is utilized to make the hybrid nanoparticle, and the hydroxyl groups function to bind the particle into the polymer, as shown in Figure 5. Alternatively, lysine alumoxane has an amino group that can be used to attach the nanoparticle to an epoxy resin.

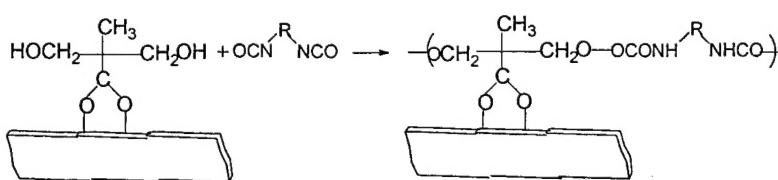


Figure 5. Reaction of alumoxane to give a nanocomposite urethane.

Alumoxane nanoparticles provide the necessary frictional resistance in a non-skid coating. Since the nanoparticles are well dispersed and chemically bound to the resin, they do not chip off or crack with wear, allowing the coating to last longer under highly abrasive conditions.

Alumoxanes in coatings can serve to introduce specific functional groups into the resin system to give it desirable properties. Generally additives with certain chemical structures are incorporated into a coating to improve specific properties. Examples include phenolics that improve corrosion resistance, phosphate esters for increased fire retardancy and bezophenone compounds to provide UV protection (Nelson 1990). These additives may leach out of the coating and are of limited use. However, the active chemical in these additives can be incorporated into the coating by chemically binding it to the alumoxane nanoparticle, which in turn is bound to the polymer resin.

In Phase I, we have incorporated phenolic groups into our urethane coatings and demonstrated that they provide added corrosion protection to the system. This was accomplished by preparing a mixed acid alumoxane, whereby one carboxylic acid (DMPA) is used to bind the nanoparticle to the polymer, while another acid (hydroxybenzoic acid, HBA) provides the phenolic group for corrosion protection and fire resistance. The mixed acid alumoxane is shown in Figure 6, where DMPA and HBA are bound to the boehmite nanoparticle. The hydroxyl groups from DMPA react with the isocyanate component of the deck coating to give a hybrid

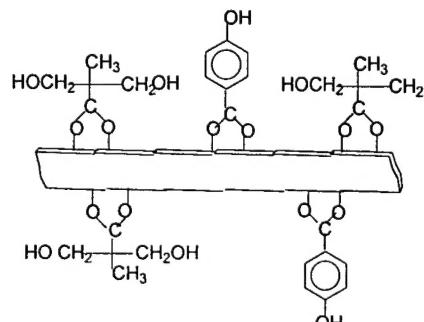


Figure 6 A mixed acid alumoxane.

urethane with well dispersed nanoparticles. The resulting coating had significantly better corrosion resistance in the Salt Fog tests.

In addition to improving the frictional resistance and corrosion protection to a non-skid coating, alumoxanes can also increase the toughness of a resin system by limiting crack propagation, absorbing impact energy in the process. As chemically bonded nanoparticles, alumoxanes also participate in crack surface bridging by applying closure forces behind the propagating crack. Unlike traditional fillers, alumoxanes are very small, have large surface area and are strongly bonded to the resin, so that their contribution to toughness is maximized. Figure 7 illustrates how a hard, strongly bonded particle can diffuse impact energy and bridge a crack, whereas easily broken or weakly bound particles provide minimal protection from cracking and chipping. Increased toughness can be measured by a series of ASTM procedures, including hardness, scratch, abrasion- and impact- resistance.

In Phase I we prepared a range of alumoxane coatings and evaluated their properties. Using ASTM test methods, we were able to demonstrate that alumoxanes significantly improved physical properties while increasing frictional resistance without chipping or cracking of the coating. The chemical properties of the hybrid resin were also improved, as shown by the increased corrosion resistance and coating stability when exposed to acids, bases and organic solvents.

### 1.3. Phase I Objectives

The overall objective of this Phase I was to develop a new hybrid organic/inorganic non-skid coating with superior physical properties, improved fire resistance and chemical stability, thereby extending the life of the coating and reducing maintenance costs. To achieve this objective, we have conducted the following tasks:

1. Synthesize and characterize alumoxane precursors (alumoxanes of PABA and DPA).
2. Incorporate the alumoxanes into Courtaulds' Proreco urethane coating system. We will use the mono-functional (PHBA) and the difunctional (DPA) alumoxanes to prepare the hybrid organic/inorganic coating. Aluminum and steel substrates will be used to evaluate the alumoxane coatings.
3. Test the coatings for several properties, including fire and corrosion resistance. Formulations will be optimized to ensure that the alumoxane incorporation does not compromise the properties of the resulting films.
4. Provide alumoxane coatings components of the best candidate for testing at naval facilities. Conduct an engineering analysis to determine the economic feasibility of using alumoxanes in non-skid coatings. Identify potential commercial applications of the non-skid, fire and corrosion resistant coating systems.

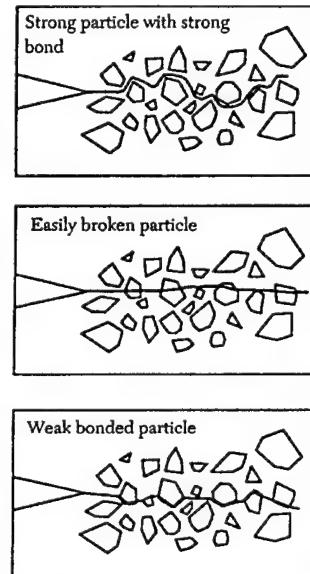


Figure 7. Crack propagation through filled resins.

5. Prepare a final report.

All of the Phase I objectives were accomplished. A tough, fire- and corrosion- resistant urethane non-skid coating was prepared with a mixed acid alumoxane and a commercial urethane marine coating. We have also provided information and exchanged ideas with a representative of Newport News Shipbuilding in order to evaluate the company's needs in a non-skid coating. Despite the fact that the alumoxane resin had excellent properties, testing of the alumoxane coating at a naval facility was deferred until formulations were optimized. Additionally, we prepared a new alumoxane specifically designed for incorporation into an epoxy-based non-skid coating.

## 2. Results of Phase I Project

In the Phase I project we prepared a series of alumoxanes, hybrid organic/inorganic reactive additives specifically designed to provide the non-skid coating with desirable properties such as fire retardancy, corrosion resistance and toughness. Since they were well dispersed and chemically bound nanoparticles, the alumoxanes also provided the coating with high frictional resistance without the chipping and cracking frequently observed with high filler, non-skid coatings.

The alumoxanes were incorporated into commercially available urethane marine coatings; these systems included a clear coat formulation and a heavily pigmented system. As we were evaluating the influence of alumoxanes on the coating's performance, we applied it on steel and aluminum panels without any special equipment used to engineer ridged surfaces. This allowed us to determine the direct contribution of alumoxanes to the resin durability and performance. The resulting alumoxane coatings met, and in some cases exceeded, the specifications listed under MIL-PFR 24667A for a non-skid coating.

Phase I results showed that:

1. Alumoxanes were prepared with the inexpensive, commercially available boehmite from Condia Vista at \$1/lb, and by the more expensive sol-gel process. This allowed the cost of alumoxanes to remain competitive, if not cheaper, than the current fillers used to make non-skid coatings.
2. Mixed acid alumoxanes were prepared and used in a coating for the first time, effectively tailoring the properties of the resin and improving its performance. One organic acid was used to bind the nanoparticle to the resin, while another acid provided the phenolic group that allowed for great improvements in corrosion resistance and fire retardancy. The concept of mixed acids is not limited to these applications. Stabilizers and UV absorbers that frequently leach out of the coating, can also be easily incorporated into the alumoxanes and made into an integral part of the resin system.
3. Alumoxanes were incorporated into urethane non-skid commercial coating formulations. However, we also demonstrated that they can be reacted with epoxy systems, broadening the range of applications, especially the market for marine coatings.

4. Toughness of the coatings was markedly improved with a 10% to 50% loading of alumoxanes. Wear resistance, measured by ASTM 4060 with an specific abrasive wheel apparatus, indicated that the alumoxane coating required 76,000 cycles to wear (expose the metal substrate), whereas the coating without alumoxane was worn after 59,000 cycles. Pencil hardness of the alumoxane coating was 8H, considerably higher than 5H of the regular coating. Unlike traditional hard fillers, alumoxanes did not compromise the flexibility of the coating; testing of coated panels by continuous bending 20 degrees at a constant rate according to ASTM F718, showed no cracking, breaking, discoloration or loss of adhesion. These results confirm that alumoxanes can greatly enhance the strength and toughness of the coating. Thus wear damage caused by arresting cables on aircraft carriers can be greatly reduced.
5. The chemical resistance of the alumoxane coatings towards organics like jet fuel and pump oil, as well as acids, was excellent. The pencil hardness remained at 8H after exposure to these reagents. Even exposure to methylene chloride, a paint stripper, barely changed the pencil hardness, though some discoloration was observed.
6. Corrosion resistance was evaluated with un-primed painted panels by the Salt Fog test. The standard urethane coating had discoloration, blisters and heavy corrosion after 600 hours of salt fog exposure, whereas the coating with 30% alumoxane had only minor corrosion along the scribe, even after 1300 hours. Obviously, the alumoxane coating has superior barrier properties that prevented the highly corrosive salt water from attacking the substrate.
7. The influence of alumoxanes on the frictional resistance of the coatings was measured. Results showed that the static coefficient of friction,  $\mu_s$ , of alumoxane coatings dramatically increased with increasing alumoxane content, until it reached the value of 1.0 (for a coating with 53% alumoxane). This value exceeded the requirements of the military specification for non-skid coatings (MIL-C-24667A). These samples were made with a clear resin formulation that did not contain filler, pigments, or non-slip agents.
8. The fire retardant properties of the alumoxane coatings were demonstrated by smoke density and oxygen index tests. Results showed that they generated less smoke than conventional coatings under flaming and non-flaming conditions. Moreover, the analysis of the smoke density as a function of time for the flaming condition showed that the coating containing alumoxane strongly inhibited the early stages of the combustion. As for the oxygen index, it was unchanged at a 25% alumoxane loading. However, at a 48% loading, the alumoxane coating required more oxygen to sustain a flame, providing an increased level of fire resistance.

## 2.1. Task 1. Synthesis and characterization of alumoxane precursors

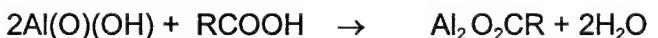
Alumoxanes are essentially inorganic nanoparticles with a covalently bounded organic shell. They are prepared by reaction of an organic acid and boehmite, an aluminum mineral. Boehmite is commercially available at \$1/lb, and can be easily dispersed in water. Alternatively boehmite can be synthesized by a more costly solgel process. Alumoxanes have been prepared with a range of organic acids, depending on the application. By choosing the appropriate organic acid, the alumoxane can be tailored to have specific functional groups,

such as hydroxyl groups for reactivity with isocyanates, or amines to react with epoxies. In this manner, alumoxanes can be chemically bound into the resin framework, providing strength, toughness and frictional resistance. Previous work at TDA has shown that alumoxanes with amino and hydroxyl functional groups can be incorporated into polyurethane, epoxy, polyesters, and polyimides.

During Phase I, we also prepared mixed acid alumoxanes, whereby more than one organic acid was used to prepare the alumoxane nanoparticles. One of the acids was generally used to provide an efficient means of attaching the alumoxane to the resin, while the other acid acted independently to improve the properties of the coating.

TDA prepared a series of alumoxanes with inexpensive, commercially available boehmite at \$1/lb and that prepared by the sol-gel process and found little difference in the product. To prepare the sol-gel, aluminum tri-sec-butoxide was hydrolyzed in boiling water in presence of aluminum nitrate. The resulting boehmite gel may be stored for months or reacted with the carboxylic acid. To prepare the alumoxane, the sol-gel was refluxed overnight with the organic acid of choice (Schubert 1995). Several alumoxanes were prepared, including alumox-HBA with hydroxybenzoic acid, alumox-DPA, with diphenolic acid, shown in Figure 8. The synthesis of the alumoxanes alumox-HBA and alumox-DPA was achieved with nearly quantitative yield. The mixed acid alumoxanes were prepared with dimethylolpropionic acid (DMPA) and HBA or DPA, will be discussed below.

The reaction was easily followed by Fourier Transform Infrared Spectroscopy (FTIR) as the carbonyl stretch absorption band of the free organic acid disappeared and a new absorption band appeared at a higher frequency (lower wavenumber) with the bidentate bonding of the carboxyl to boehmite. The general equation for the synthesis of alumoxane is



A typical FTIR spectrum of an organic acid and its alumoxane is shown in Figure 9 for DPA and alumox-DPA. The carbonyl band at  $1701\text{ cm}^{-1}$  of the free diphenolic acid had disappeared and a new absorption at  $1578\text{ cm}^{-1}$  indicated the formation of the alumoxane linkage in the product. This confirmed that the reaction between the acid and boehmite went to completion and that no purification or separation step was necessary. An analogous result was found when alumox-HBA was synthesized; the acid carbonyl absorption at  $1675\text{ cm}^{-1}$  was replaced with the alumoxane absorption at  $1555\text{ cm}^{-1}$ .

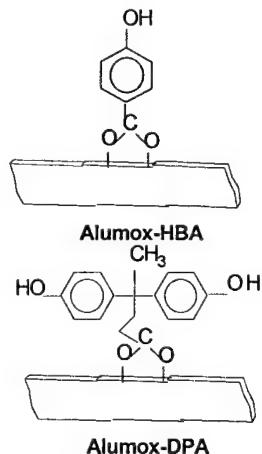


Figure 8. Structures of alumoxanes with phenolic groups.

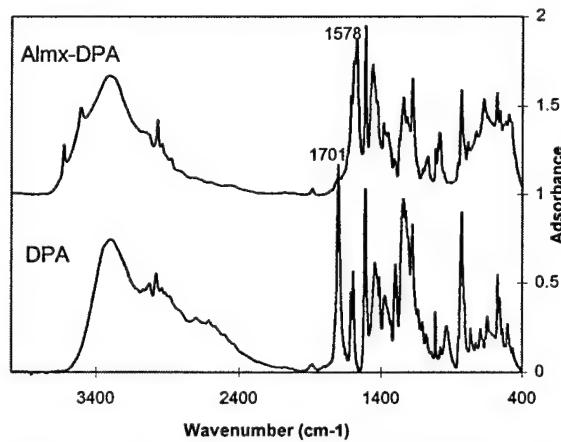


Figure 9. FT-IR spectra of diphenolic acid (DPA and alumoxane-DPA)

The alumoxanes were also characterized by Thermogravimetric Analysis (TGA) (Figure 10) to determine their thermal stability. The TGA indicated that alumoxane HD 10 (prepared with acids made up of 10% DMPA and 90% HBA) was stable to temperatures as high as 375°C. Thus incorporating alumoxanes in the resin is expected to stabilize the non-skid coating used for aircraft carrier deck applications, where aircraft exhaust gases can damage a typical organic coating.

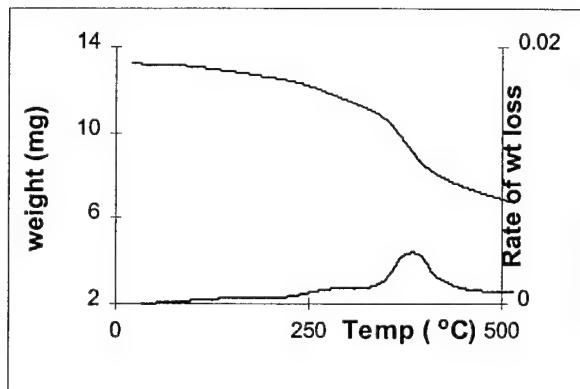


Figure 10. TGA of HD Alumoxane.

The alumoxanes chosen for the initial preparation of non-skid coatings were of the phenolic type, with alumox-HBA and alumox-DPA (Figure 8) containing one and two phenolic groups respectively. Phenolic moieties were selected because of their fire retardant properties. Moreover, previous work at TDA has shown that coatings containing alumox-HBA were remarkably corrosion resistant when tested in the salt-fog chamber. Both fire retardancy and corrosion resistance are critical in making non-skid coatings for air-craft carriers.

### Mixed acid alumoxanes

Mixed acid alumoxanes, shown in Figure 6, with a phenolic group and an aliphatic diol, were also prepared. This was carried out in order to improve the reactivity of the alumoxane nanoparticle and facilitate its incorporation into the polymer framework. Aliphatic diols are significantly more reactive towards isocyanates than their aromatic counterparts. Thus alumoxanes were prepared with a combination of the phenolic acids such as hydroxybenzoic acid (HBA) or diphenolic acid (DPA) and an aliphatic diol acid, like dimethylopropionic acid (DMPA) or hydroxymethylbenzoic acid (HMBA). An illustration of an alumoxane nanoparticle with a mixed acid composition is shown in Figure 6. Thus five reactive alumoxanes, listed in Table 1, were prepared for incorporation into a urethane resin, with phenolics to provide corrosion- and fire-resistance to the coating. The synthesis of the mixed acid alumoxanes was carried out as described above for the alumoxanes, initially refluxing boehmite and the first acid for two hours before addition of the second acid.

Table 1. Composition of mixed acid alumoxanes

Alumoxane	DMPA	HMBA	HBA	DPA
HD10	10		90	
HD30	30		70	
HD50	50		50	
DD10	10		90	90
HH10		10		

The FT-IR spectra of these materials, with the exception of alumoxane HH10, showed full conversion of the acid to the alumoxane, and that two acids were present on the surface of each alumoxane. Alumox-HH10 contained unreacted HMBA acid, suggesting that the reaction between HMBA and boehmite is very slow. Therefore, alumox-HH10 was set aside and the other four mixed acid alumoxanes were evaluated.

The mixed acid alumoxanes were highly reactive with isocyanates such as MDI; the isocyanate consumption (determined by quantitative FTIR analysis) after one hour of reaction was proportional to the DMPA concentration on the alumoxane. Therefore, TDA was able to

develop novel mixed alumoxanes that combined high reactivity toward isocyanates, while contributing good fire resistant properties.

X-Ray Diffraction (XRD) was used to examine the presence of crystallinity in the alumoxane hybrid. Boehmite has a distinct crystalline pattern shown in Figure 11. The XRD of the mixed acid alumoxane confirmed the presence of significant crystallinity in the alumoxane nanoparticle. Definitive crystalline patterns showed some short range order typical of boehmite at high values of  $2\theta$ , and a complex crystalline order at low values of  $2\theta$ . High crystallinity generally leads to reduced permeability and good barrier properties. These characteristics, in turn, lead to superior corrosion protection and resistance to chipping and cracking. Indeed, these properties were observed with the alumoxane coatings prepared at TDA.

## 2.2. Task 2. Incorporation of alumoxanes into non-skid coatings

The alumoxanes prepared in Task 1 were incorporated into commercial coating formulations. We used International Paint's marine coatings currently applied on ship decks; they include Proreco urethane coating systems as:

1. Two components clear polyurethane Proreco 508 (PRA600 + PRA560)
2. The two components non-skid polyurethane coating Proreco 469 (PRA460 + PRA461).

Alumoxanes HD10, HD30, HD 50 (prepared with HBA respectively) and DD10 (prepared with 10% DMPA and the remainder with DPA) were dispersed at several levels in the clear coat Proreco 508, and in the non-skid formulation Proreco 469, used to paint steel coupons. The clear coating Proreco 508 did not contain any solid additives, while Proreco 469 was a complete formulation for non skid-coatings with additives, pigments, filler, and non slip-agents. The alumoxane-polyurethane coatings were prepared by high shear mixing of the alumoxane with the isocyanate component of the formulation (PRA 600 or PRA 461), followed by the addition of the second component of the coating (PRA 560 or PRA 460).

Coatings made from alumoxanes and the clear polyurethane Proreco 508 were used to acquire the basic information regarding the effect of alumoxanes on the physical-chemical, thermal, and mechanical properties of the resulting films. The first set of coatings, series S in Table 2, were prepared with HD10 alumoxane (the mixed acid alumoxane with 10% of the total organic content made up of aliphatic DMPA and 90% phenolic HBA). Physical appearance, ability to homogeneously

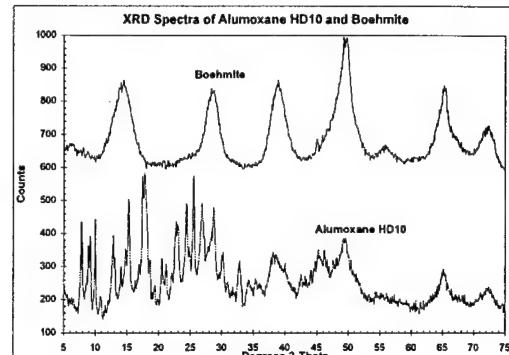


Figure 11. XRD of mixed acid alumoxane.

Table 2. Coatings prepared with alumoxane HD10.

Coating ID	% HD10 (w/w)	Coating description
S01	0	clear homogeneous
S02	8	irregular film
S03	16	irregular film
S04	27	homogeneous
S05	32	homogeneous smooth film
S06	36	homogeneous smooth film
S07	43	homogeneous smooth film
S08	48	homogeneous smooth film
S09	53	film compromised
S10	56	film compromised
S11	64	film compromised

disperse the alumoxanes and film forming properties were used for the initial screening. Results shown in Table 2 indicated that as much as 48% (w/w) alumoxane could be incorporated into the coating without any detrimental effect on the film-forming properties of the resin.

Additional coatings were prepared using alumoxanes with increasing aliphatic content. These included series F, with HD30 (30% aliphatic and 70% phenolic groups) and series G, with HD50 (50% aliphatic and 50% phenolic groups) shown in Table 4 and Table 3 respectively. Finally, the alumoxane DD10 (with 10% DMPA and 90% diphenolic acid, DPA) were used to prepare coatings in series H (Table 5), also with good film forming properties.

The film forming properties of the alumoxane resin appeared to be independent of the ratio of aliphatic to phenolic components that made up the mixed acid alumoxane. Although coatings made up with less than 20% alumoxanes may require reformulation to improve the dispersion of alumoxane nanoparticles, the coatings were generally homogeneous and smooth with as much as 48% alumoxane.

The complete non-skid formulation Proreco 469 with additives, pigments, fillers, and non slip-agents, was used to verify the compatibility of alumoxanes with the other components of the coating, and to test the properties of the final product. Table 6 lists the description of the coatings prepared with Proreco 469 and alumoxane HD10.

Alumoxane HD10, HD30, HD 50, and DD10 were compatible with both Proreco 508 and Proreco 469 formulations, and gave uniform coatings with good film properties. The coatings with 36 or 48 wt % of alumoxane were highly homogeneous, showed excellent film-forming properties, and had good physical and mechanical properties. The sample of the coating shown in the photograph in Figure 2 was prepared with 48% alumoxane HD10, demonstrating the film's finely textured and homogeneous appearance.

### 2.3. Task 3. Testing the alumoxane non-skid coatings

Alumoxane resins were prepared and evaluated as non-skid coatings with improved properties. Since alumoxanes were well dispersed, reactive nanoparticles with tailored chemical structures, we expected improvements in several physical and chemical properties of the coating. In particular, we were interested in increased toughness which generally leads to wear resistance

Table 3. Coatings prepared with alumoxane HD50.

Coating ID	% HD50 (w/w)	Coating description
G01	36%	homogeneous smooth film
G02	48%	homogeneous smooth film

Table 4. Coatings prepared with alumoxane HD30.

Coating ID	% HD30 (w/w)	Coating description
F01	36%	homogeneous smooth film
F02	48%	homogeneous smooth film

Table 5. Coatings prepared with alumoxane DD10.

Coating ID	% HD10 (w/w)	Coating description
H01	36	homogeneous rough film
H02	48	homogeneous rough film

Table 6. Coatings prepared with commercial non-skid Proreco 469 and alumoxane HD10.

Coating ID	% HD10 (w/w)	Coating description
S40	0	homogeneous rough film
S41	27	homogeneous rough film

and a longer useful lifetime of the coating. Toughness was measured by ASTM methods such as the pencil hardness and abrasion resistance. Other properties that alumoxanes were expected to improve included corrosion resistance, measured by the Salt Fog test and fire retardancy, described by the oxygen index and the smoke index. Non-skid characteristics of the alumoxane coatings were measured by static coefficient of friction.

The alumoxane-urethane coatings were also fully characterized by FTIR spectroscopy to ensure that the alumoxanes were fully reacted with the isocyanate to form the urethane linkage that bound the nanoparticle to the resin matrix. Thermal analysis (including differential scanning calorimetry, and thermogravimetric analysis) was conducted to evaluate the influence of alumoxanes on the thermal stability of the coating.

### 2.3.1. Toughness

#### 2.3.1.1 *Pencil hardness*

The pencil hardness of alumoxane-polyurethane non-skid coatings was measured according to ASTM 3363. International Paint's Proreco urethane coating was used as the resin system for the incorporation of alumomxanes. Several mixed alumoxanes were evaluated. The results shown Table 7 in indicate that the hardness of the hybrid coatings is significantly increased with increasing alumoxane content, going from 5H for the coating without alumoxane (sample S01) to 8H for the coatings with 48% alumoxanes.

Table 7. Pencil hardness of alumoxane resins (ASTM 3363).

Sample	Alumox content (%)	Pencil hardness
S01	0	5H
S05	32	7H
H01	36	6H
F02	48	8H
G02	48	6H
S08	48	8H

#### 2.3.1.2 *Flexibility*

The coating flexibility was tested over a 5 inches mandrel according to ASTM F 718. Coated steel panels were bent at 20 degrees at a constant rate, and examined for cracking, breaking or loss of adhesion immediately after bending (specification in Mil Spec-C-24667A; 4.6.11). The alumoxane coatings tested showed no cracking, breaking, discoloration, or loss of adhesion after being bent over the 5 inches mandrel. The addition of as much as 48% alumoxane in the hybrid coatings resulted in good flexibility.

### 2.3.1.3 Wear resistance

Abrasion resistance of the alumoxane urethane coatings was evaluated by the Tabor Abraser test (ASTM 4060). Analysis was carried out on 4"x 4" aluminum coated panels, using two resilient calibrase wheels (CS-17, BYK Gadner), each mounted with 1000 pound load. The coating thickness and weight loss were measured. The samples tested included a clear coat optimized formulation (S01) and urethane coatings with alumoxane ranging from 16% to 36%. Figure 12 shows the panels with wheel abrasion of the clear coating after 6400 cycles and exposure of the steel substrate (Figure 12, left) and the 30 % alumoxane coating after 10,000 cycles showing minimal wear (Figure 12, right). Since the hybrid alumoxane coatings have a higher density than the organic urethane coatings, the abrasion resistance was evaluated using measurements for the loss in thickness, rather than weight loss.

The results shown in Table 8 indicate that alumoxanes improved the wear resistance of the coating when used at levels around 16%. At levels as high as 36%, the urethane film lost mechanical strength. However, during the entire abrasion process, the 16% (w/w) alumoxane coating showed a significant reduction in frictional wear, when compared to the clear resin. Overall, the 16% (w/w) alumoxane coating required almost 20,000 more abrasion cycles than the clear coat to reach the metal surface.

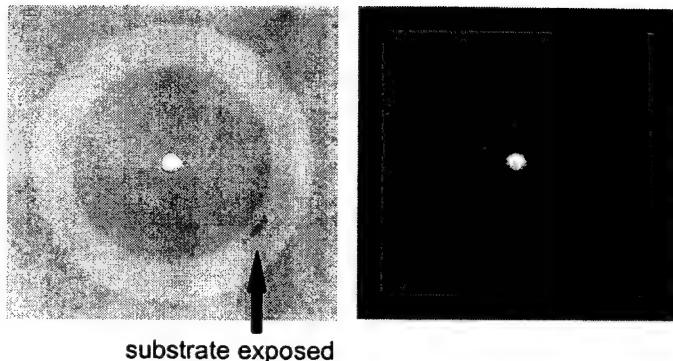


Figure 12. Coatings showing wear by Tabor Test. Clear coating (left) alumoxane coating (right).

Table 8. Thickness loss after several cycles on the Tabor Abraser by ASTM 4060 (measured in mil).

loss after a number of cycles	S01 0% alumox	S03 16% alumox	S06 36% alumox
4,000	1.9	1.3	0.5
8,000	2.6	1.6	1.6
12,000	3.9	2.3	2.4
20,000	5.3	3.3	4.3
40,000	8.1	6.9	9.9
52,000	9.9	8.6	-
60,000	10.8	9.8	-
64,000	-	10.6	-
Wear cycles/mil	5463	5619	-
Wear cycles to metal surface	59,000	76,000	-

### 2.3.1.4 Static friction coefficient ( $\mu_s$ )

The static friction coefficient ( $\mu_s$ ) of the alumoxane-polyurethane films has been measured with a Coefficient of Friction Tester according to the ASDM D1894. Results show that  $\mu_s$  of alumoxane-polyurethane coatings dramatically increased with increasing alumoxane content, until it reaches the value of 1.0 with 53%(w/w) alumoxane, as shown in Figure 13. This value is above the requirements of the military specification for non-skid coatings (MIL-C-24667A). These samples were formulated with the clear Proreco 508 resin, which does not contain filler, pigments, or non-slip agents.

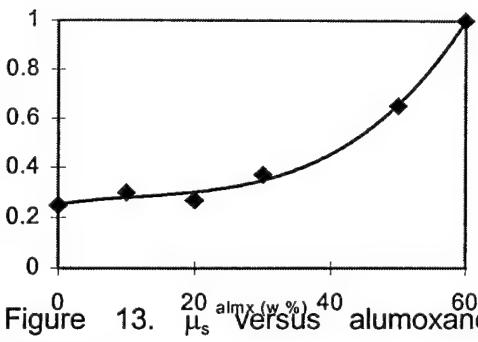


Figure 13.  $\mu_s$  Versus alumoxane content.

### 2.3.2. Flammability and Thermal Properties.

The thermal stability and behavior were examined by DSC and TGA. Flammability properties were measured by the smoke density and oxygen index.

#### 2.3.2.1 Differential Scanning Calorimetry (DSC)

A set of clear coatings (prepared with Proreco 508) containing an increasing amount of alumoxane HD10 (with the organic content made up of 10% DMPA and 90% HBA) were analyzed by DSC to evaluate the influence of alumoxanes on the phase behavior and physical properties of the polyurethane matrix.

Using a Shimadzu DSC-50 to heat samples at 10°C/ min. from 20°C to 450°C, the DSC of the clear coating Proreco 508 (sample S01) showed a clear melting peak at 334°C, and a glass transition (Tg) in the range of 50°C to 70°C. Samples S03, S04, S06, S08, and S09, containing increasing amounts of alumoxane HD10, had approximately the same melting point suggesting that alumoxane HD10 did not alter the crystalline phase of the polymeric resin (Table 9). The DSC curve of samples with alumoxane content higher than 40% (S06, S08, and S09) showed the presence of some pre-melting peaks in the range of temperatures 150°C to 290°C, indicating the presence of oligomeric fractions. This suggested that alumoxanes effectively behaved as macro-monomers, with the nanoparticles included in the middle of the growing polymer chains. As the concentration of alumoxane increased, the chain length between two macro-monomers decreased. These short polymeric chains between two hybrid macro-monomers had a lower melting point.

The glass transition of the amorphous part of the polyurethane resin increased with the alumoxane concentration. This is an indication that the coating became stiffer and harder with increasing alumoxane content.

Table 9. Thermal properties of the coating measured by DSC.

Coating ID	alumox (wt %)	m.p. (°C)	Tg (°C)	pre-melting peaks (°C)
S01	0%	334	58	193
S03	16%	331	-	-
S04	27%	333	62	-
S06	36%	339	64	290
S08	48%	329	74	150 - 287
S09	53%	325	75	157-273

Thus the presence of alumoxanes in the resin matrix has led to increased stabilization by cross-linking through the nanoparticle. A stiffer, stronger resin resulted with increasing alumoxane content, indicating that toughness can be increased through the incorporation of alumoxanes.

### 2.3.2.2 Thermogravimetric Analysis (TGA)

A set of clear coatings (Proreco 508) containing an increasing amount of alumoxane HD10 was subjected to Thermogravimetric Analysis (both under nitrogen and air atmospheres on a Shimadzu TGA-50 analyzer) to evaluate the influence of alumoxanes on the temperature and mechanism of the polyurethane thermal degradation. Under nitrogen, there was little difference in the TGA of all the samples examined (from sample S01, with no alumoxane to sample S08, with 53% alumoxane).

Under a dry air flow, all the samples degraded and lost weight in two steps or processes. Each degradation process was characterized by an onset temperature, a mid-point temperature, and a weight loss, as shown in Figure 14. The first process corresponded to the degradation of the organic resin in presence of air, and started around 275°C; the second step corresponded to the combustion of the resin in oxygen, beginning at about 450°C.

The weight loss at 450°C due to thermal degradation of the coating is plotted in Figure 15, showing the influence of the alumoxane content on the thermal stability of the coating. We need to mention that we expected a reduction in weight loss for the samples containing alumoxanes simply because alumoxanes contain a small fraction of non-degradable, non-combustible inorganics. However, weight loss data based on the organic fraction exclusively, also demonstrated that the increasing content of alumoxanes led to a reduction in weight loss and an increase in the thermal stability of the coating. The upper curve in Figure 15 demonstrated that the coating without alumoxane degraded upon heating in air, losing 74% of its weight by the time the temperature reached 450°C, whereas the coating with 53% alumoxane lost only 54% of its weight at that temperature (based on organic fraction only).

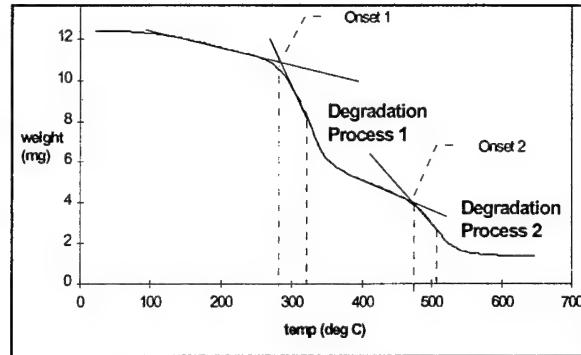


Figure 14. Weight loss as thermal degradation measured by TGA.

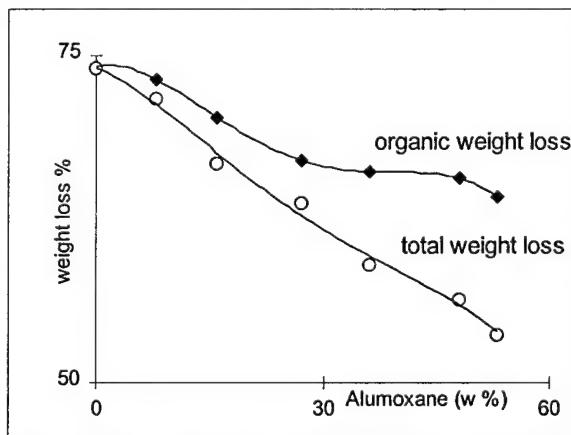


Figure 15. Influence of alumoxane content on thermal degradation of the coating.

Generally a coating exposed to air at high temperatures degrades through polymer chain scission and evaporation of the volatile fraction, leading to weight loss, film cracking, and failure in mechanical strength. This behavior is observed as "degradation process 1" of the TGA curve (Figure 14), starting at 275°C and ending at 450°C. At higher temperatures, total oxidation takes place, followed by the conversion of the remaining organic fraction to volatiles and total weight loss ("degradation process 2", 475°C to 600°C). Table 10 lists the coating weight loss for each of these processes. As the alumoxane content was increased, thermal degradation and weight loss of the coating during "degradation process 1" was reduced from 84% for the coating without alumoxane, to 50% for the coating with as much as 53% alumoxane. Such a large reduction in degradation and weight loss implies that the film is less likely to lose its mechanical properties in that temperature range when alumoxanes are present in the coating system.

Thus, the incorporation of alumoxanes into the resin formulation results in the additional benefit of providing thermal stability to the coating over temperatures ranging from 275°C to 475°C, reducing degradation that leads to accelerated mechanical failure. This is expected to extend the durability of the coating and aid in meeting the military specification of lasting 10,000 landings per coating lifetime.

### 2.3.2.3 Smoke Density

The Smoke Density Test (ASTM E-622) was conducted on a clear urethane film (S01) and one containing alumoxanes (S05). The maximum smoke density ( $D_{mc}$ ), and the calculated smoke density as a function of time, were measured at SGS U.S. Testing Company.

The results shown in Table 11 indicate that the coating containing alumoxane HD generates less smoke than the coating without alumoxane both under the flaming, and non-flaming conditions. This suggests that alumoxanes bearing hydroxy-benzoic acid can effectively improve the fire retardancy properties of polyurethane-based non-skid coatings. Moreover, the analysis of the smoke density in function of time for the flaming condition showed that the coating containing alumoxane, strongly inhibits the early stages of the combustion. In fact the smoke densities ( $D_s$ ) of the alumoxane coating, after 1.5 and 4 minutes were considerably less than those of the clear coating (S01).

Table 10. Weight loss from the thermal degradation of alumoxane coatings over a wide range of temperatures.

% alumox (w/w)	% weight loss Process 1 (275-400°C)	% weight loss Process 2 (400-600°C)	weight loss ratio *
0	84	16	5.3
8	80	18	4.4
16	79	17	4.5
27	72	23	3.1
36	63	27	2.4
48	60	26	2.3
53	50	34	1.5

\* weight loss ratio =  $\frac{\% \text{ weight loss Process 1}}{\% \text{ weight loss Process 2}}$

Table 11. Smoke Density values for alumoxane coatings

Alumoxane (wt%)	$D_{mc}$ non-flaming	$D_{mc}$ flaming
0%	103.1	129.2
32%	92.9	112.2

Alumoxane (wt%)	$D_s$ after 1.5 hrs	$D_s$ after 4 hrs
0%	20.2	106.5
32%	12.3	81.8

### 2.3.2.4 Oxygen index

The oxygen index (OI) of the alumoxane-polyurethane coatings was measured at SGS U.S. Testing Company, according to ASTM D-2863. The analysis measured the amount of oxygen required to sustain a flame in an oxygen/nitrogen environment for a specified period of time. We incorporated two different alumoxanes in the Proreco 469 formulation currently in use on ship decks, containing filler, pigments, and non-slip agents. The results indicated that at a 25% alumoxane loading, the OI value was unchanged and that the coatings had the same flammability (Table 12). However, at a 48% loading, the alumoxane coating requiring more oxygen to sustain a flame, providing an increased level of fire resistance.

Table 12. Oxygen Index of alumoxane coatings.

Sample	Alumoxane type	Alumoxane content	OI
S40	-	0%	27
S41	HD10	27%	27
S48	DD10	48%	32

### 2.3.3. Corrosion resistance

The effect of alumoxane coatings on the corrosion prevention of metal surfaces was evaluated on an aluminum substrate in the absence of any epoxy primer. Aluminum panels (Al 7075-T6) were coated with the alumoxane urethane resins after cleaning with acetone and an alkaline solution. Coatings were also prepared with International Paint's Proreco urethane coatings.

Results of the Salt Fog test (ASTM B117) indicate that the presence of alumoxanes significantly reduced corrosion, and in some cases prevented it completely. As expected, the unprimed panel with urethane coating had discoloration, blisters and corrosion beyond the scribe after 600 hours, whereas the coating with 30% alumoxane had minor corrosion along the scribe. However, coatings with 40% alumoxanes were stable well beyond the 1300 hours of the experiment, with no blisters or discoloration, as shown in Figure 16.

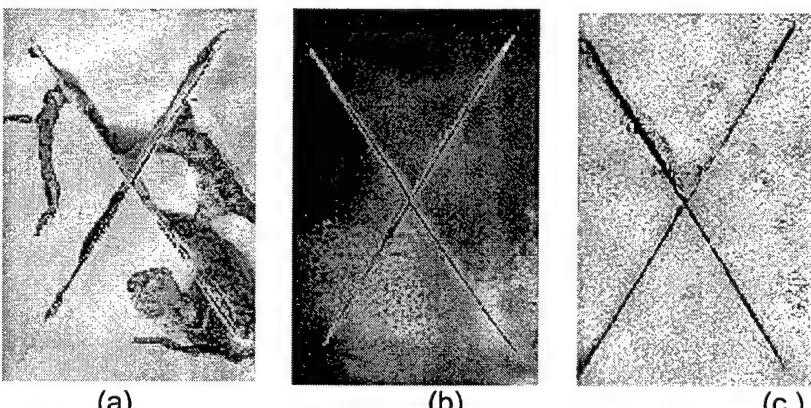


Figure 16. Panels exposed to Salt Fog tests (a) urethane coating after 600 hours (b) 30% alumoxane in urethane after 600 hours (c) 40% alumoxane in urethane after 1300 hours.

### 2.3.4. Chemical resistance

The chemical resistance of polyurethane-alumoxane coatings was tested in accordance to ASTM D 1308. Coated steel coupons were exposed for 30 minutes to JP-8 jet fuel, pump oil, 10% solution of acetic and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). There were no changes in any of the samples after exposure to JP-8 fuel and pump oil (Table 13). Exposure to 10% acetic acid did not result in discoloration or blistering, but a change of gloss was observed in samples H01 (prepared with alumoxane DD10, a mixed acid alumoxane with 90% DPA and 10% DMPA) and

G02 (prepared with alumoxane HD50, a mixed acid alumoxane with 50% HBA and 50% DMPA). The hardness of sample H01 slightly decreases after acetic acid exposure.

Although dichloromethane is very aggressive with polyurethane coatings and is used as a paint stripper, some of the hybrid alumoxane-polyurethane coatings made at TDA performed very well in presence of  $\text{CH}_2\text{Cl}_2$ . In fact, the clear coating with no alumoxane showed the presence of an halo and softened from hardness 5H to hardness 4H after  $\text{CH}_2\text{Cl}_2$  exposure, while two of the alumoxane-polyurethane formulations (S08, and F02) did not change hardness (8H) and showed only a little discoloration, but no blisters or swelling. Coatings with a too high an alumoxane content were not resistant to dichloromethane.

Table 13. Chemical resistance of alumoxane coatings, measured by pencil hardness, according to ASTM D1308.

Sample	virgin coating	After exposure to JP8	After exposure to pump oil	After exposure to 10% acetic acid	After exposure to methylene chloride
S01	5H	5H	5H	5H	4H halo, discoloration
S05	7H	7H	7H	7H	4H little discoloration
S08	8H	8H	8H	8H	8H slight discoloration
F02	8H	8H	8H	8H	8H little discoloration
G02	6H	6H	6H	6H reduced gloss	< 1H large discoloration swelling & blisters
H01	6H	6H	6H	5H reduced gloss	2H discoloration small blister

#### 2.4. Task 4. Choosing the best candidate and providing samples to Naval facility

In the previous task, we evaluated the performance of several alumoxanes added to the coating formulation in loading ratios that ranged from 8% to 53% (w/w). Alumoxanes, as hybrid additives, generally improved the performance of the coating, and the degree of improvement was dependent on the loading of the hybrid additive. The coating properties were also influenced by the aliphatic to phenolic ratio in the alumoxanes.

Coatings were prepared with alumoxanes using the proposed carboxylic acids. They included the reactive aliphatic dimethylol propionic acid (DMPA) or hydroxymethyl benzoic acid (HMBA). We also attempted to prepare coatings with alumoxanes of phenolic acids like hydroxybenzoic acid (HBA) and diphenilic acid (DPA) because they contribute to the fire-resistance and corrosion inhibition of a coating. Since the phenolic alumoxanes were not very reactive towards isocyanates used to make urethane coatings, we prepared "mixed acid alumoxanes" with a fraction of the phenolic groups substituted by DMPA groups to bind the alumoxane nanoparticle to the urethane polymer framework, while still providing a significant phenolic content.

The HBA and DMPA mixed acid alumoxane, designated as HD alumoxane, were prepared with partial substitution of HBA by DMPA. For example, HD 10 was prepared with 90% HBA and 10% DMPA, based on molar ratios of the acids. Similarly HD30 had 70% HBA and 30% DMPA. Another mixed acid alumoxane, DD10, was made up with 90% DPA and 10% DMPA. Thus phenolic groups on alumoxanes could be chemically bound to the urethane polymer.

During the six month Phase I project, we have prepared and tested several mixed acid alumoxane. A summary of the results is shown in Table 14. Preliminary analysis indicated that coatings with alumoxanes containing HBA easily formed homogeneous films, with better chemical and corrosion resistance than those prepared with DPA. However, coatings with alumoxanes containing DPA had slightly better fire resistance.

The influence of the aliphatic DMPA content that binds the particle into the coating was also examined. It appeared that 10% aliphatic provides adequate binding, though abrasion resistance improved with increased DMPA content. In Phase II, if granted, we will re-examine these ratio in order to maximize the benefits derived from alumoxane additives.

Table 14. Summary of phase I results. Properties of alumoxane coatings.

Almx Type	none	HD10	HD10	DD10
Almx content (wt %)	0%	32 - 36%	43 - 48%	48%
<b>Toughness</b>				
Pencil Hardness	5H	7H	8H	7H
Coeff. of friction ( $\mu_s$ )	0.25	0.37	0.65	-
Abrasion resistance(mil) <sup>1</sup>	1.9	0.5	1.7	2.1
<b>Flammability</b>				
Oxygen Index	32	22	22	32
Smoke density $D_{mc}$ <sup>2</sup>	129.2	112.2	-	-
Smoke density $D_{mc}$ <sup>3</sup>	103.1	92.9	-	-
Org. loss at 400°C (%)	74.2	66.2	65.6	-
<b>Corrosion resistance<sup>4</sup></b>				
	delamination total at 600 hr, corrosion under coating	Corrosion only along the scribe after 600 hr	Corrosion only along the scribe after 1300 hr	-
<b>Chemical resistance</b>				
Resistance to fuel JP8	excellent	excellent	excellent	excellent
Resistance to pump oil	excellent	excellent	excellent	excellent
Resistance to acetic acid	excellent	excellent	excellent	change in gloss
Resistance to fuel $CH_2Cl_2$ (Hardness)	discoloration, 4H	discoloration 4H	slight discoloration 8H	discoloration, small blisters, 2H

<sup>1</sup> thickness loss after 4000 cycles (mil.)

<sup>2</sup> under flaming conditions

<sup>3</sup> non flaming conditions

<sup>4</sup> Salt Fog Test

These preliminary results demonstrated that the incorporation of alumoxanes into coatings improved the overall material properties, while allowing the formulator to tailor the coating to meet specific needs. For example, optimum fire resistance is obtained with the high DPA content alumoxane, like DD10, whereas corrosion inhibition is best achieved with HBA and the alumoxane HD10. Similarly, toughness and chemical resistance are generally improved with a high alumoxane loading of HD10. This flexibility in formulation and corresponding performance parameters is advantageous since non-skid coatings are used in a broad range of applications, with specific needs.

### **3. Phase II Objectives**

The goal of Phase II is develop hybrid alumoxane non-skid coatings with increased toughness and extended lifetime, allowing the landing deck coating of an aircraft carrier to last 10,000 landings, as specified by MIL-PFR24667A. The U.S. Navy and the marine coatings industry are very interested in innovative non-skid coatings, so that Phase II work will be designed to meet their needs while facilitating the technology transfer to commercial industrial applications. Therefore, the development of non-skid coatings will also be directed to serve civilian applications such as pool decks, walkways and casements for outdoor machinery that require surfaces with high frictional resistance.

#### **3.1. Phase II Technical Objectives**

The overall objective of this research is to develop alumoxane non-skid coatings with substantially improved properties. This will be accomplished by the use of hybrid alumoxane reactive additives. In Phase I we demonstrated that organic/inorganic nanoparticles can be incorporated into urethane and epoxy coatings, giving them improved properties. In Phase II, we will prepare and improve these resins. We will reformulate the coatings to accommodate the alumoxane nanoparticles, giving durable films with optimized properties.

The alumoxanes will be incorporated into urethane and epoxy resin systems, with coatings formulations adjusted to give the best material properties. Four areas will be targeted for improvement; these include the wear and frictional properties through increased toughness, flammability and high temperature stability, chemical resistance towards fuels and solvents, and corrosion inhibition for steel and aluminum substrates. Testing will be conducted on the resulting coatings to evaluate the best candidates.

TDA will work closely with Air Products and Chemicals (APCI) to scale up the alumoxane synthesis technology. This work is already under way and is already funded by APCI. Air Products manufactures and markets additives and monomers for the plastics and coatings industry, and is our partner in the development of processes to manufacture alumoxanes. We will also work in conjunction with International Paint, one of the largest producer of advanced coatings, to develop the alumoxane urethane and epoxy resin systems. In Phase III, we will license the resin technology to a large manufacturer of paints and coatings like International Paint. TDA will provide formulated resins to Newport News Shipbuilding (NNS) for evaluation. As a potential customer, NNS may make recommendations for improvement; TDA will work closely with NNS to develop a coating that meets its needs.

The Phase II research consists of five tasks, with the overall objective of replacing the current non-skid coating with a tough, wear resistant, low flammability system. In Task 1 we will synthesize the diol and the amine terminated alumoxane reactive additives and determine the best way to maximize their yield. In Task 2, TDA will prepare and evaluate the formulated resin mixtures, establishing the best approach to incorporate the alumoxanes. An experimental design will be used to determine concentrations at which the alumoxanes will provide the greatest improvement in performance; processing conditions will be established in a manner as to maximize the benefits of incorporating nanoparticles in the resin matrix. We will test the coatings in Task 3 and reformulate them with the goal of improving properties like toughness, fire retardance, corrosion inhibition and chemical resistance. An engineering analysis will be conducted to estimate the costs of materials under evaluation in Task 3. Finally production of the most promising materials will be scaled up in Task 4. Initial scale-up of alumoxane production will be carried out at TDA, and Air Products will evaluate the manufacturing process at their plants. Task 4 will also include the scale-up of resin production and ready-to-use formulations at TDA and at the International Paints facilities.

### **3.2. Phase III Commercialization**

TDA had assembled a team of producers and manufacturers, along with its staff of experts on resins and nanoparticle science to bring the alumoxane technology to market. Air Products, a major producer of plastics additives, with annual sales of \$3 billion, is interested and has signed an agreement with TDA to develop its alumoxanes as additives in resins, coatings and adhesives. Air Products and Chemicals will be the commercial producer of alumoxane additives and the supplier of the additives to International Paint. International Paint will be involved in the development, manufacturing and sale of the hybrid alumoxane resins and their application to non-skid coatings for a wide range of applications.

### **4. Commercial Potential**

Alumoxane non-skid coatings under development at TDA have a broad range of applications. These include architectural systems like pool decks, stairways and floors in patios and garages. The marine applications of alumoxane coatings include recreational boats and walkways on beach areas. A major application of alumoxane non-skid coatings is as machinery casements requiring surface traction. As such, the hybrid coatings can also provide a high degree of corrosion protection. In fact, since alumoxane coatings have high thermal and chemical stability and can be applied to a variety of substrates, their commercial potential is very promising.

Current non-skid coatings used on aircraft carriers and other specialty applications cost about \$60/gal (approximately \$7/lb). Alumoxanes can be prepared at \$1-2/lb, well below the cost of colloidal silica and high traction siloxane elastomers (\$4-6/lb) currently used in non-skid formulations, or flame retardants (\$4/lb), UV absorbers (\$3-6/lb) and other additives used in coatings. Replacing some of these specialty materials can lead to a low cost, non-skid coating for a broad range of applications.

## 5. Summary and Conclusions

In this Phase I project, we have prepared a series of hybrid alumoxane reactive additives and incorporated them into urethane and epoxy resins to give coatings with improved properties. Non-skid coatings were prepared and tested for their physical and chemical properties. Alumoxanes were found to significantly increase the coefficient of friction without the addition of sand and other hard particles. The coating toughness was also improved, as demonstrated by tests measuring abrasion resistance, hardness and flexibility. The presence of the alumoxanes also improved the thermal stability of the resin and reduced the flammability of the coating. Additionally, alumoxanes contributed to an increase in chemical resistance to organic solvents and fuels. Finally, corrosion studies conducted under a salt fog environment indicated that alumoxanes provide some protection to the substrate, substantially reducing the degradation of the substrate in the corrosive environment.

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